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INFLUENCE OF SURFACE SILICA IMPURITIES ON THE
SINTERING BEHAVIOR OF ALUMINA POWDERS

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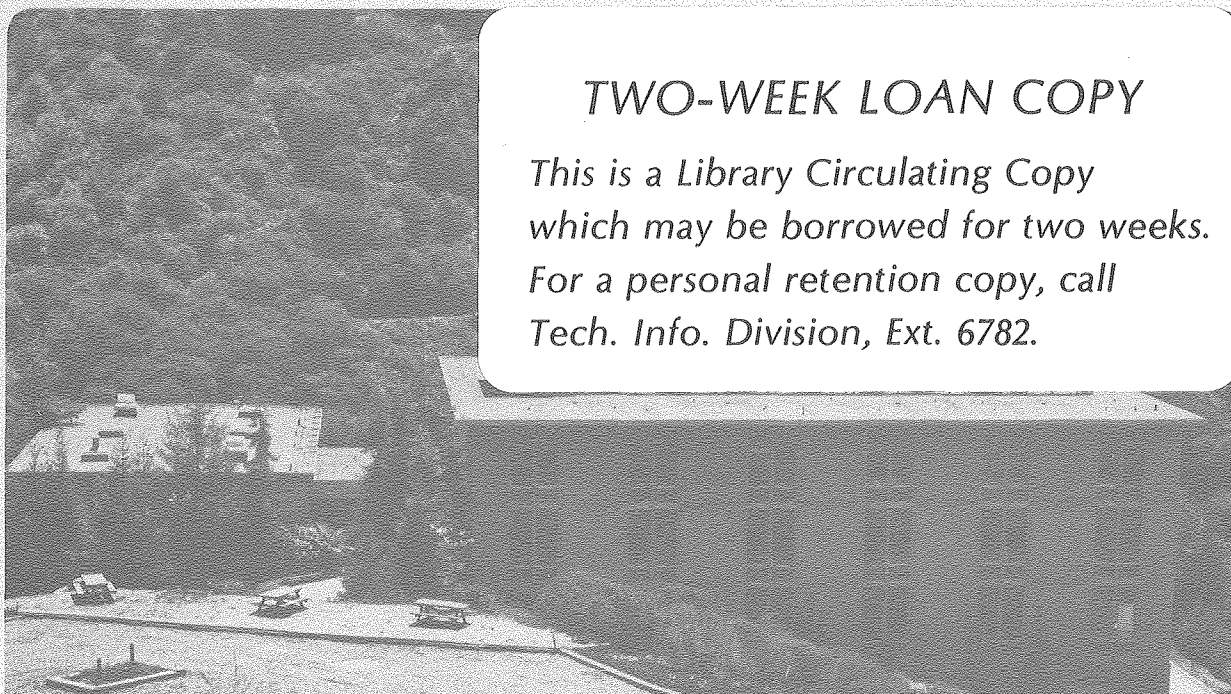
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INFLUENCE OF SURFACE SILICA IMPURITIES
ON THE SINTERING BEHAVIOR OF ALUMINA POWDERS

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ABSTRACT

The filtering, pressing and sintering behavior of an alumina powder with and without silica impurity on surface has been studied. When silica is removed from surface by HF-treatment and compactibility is considerably enhanced due to the different acidity/basicity nature of the OH of the hydroxyl layers. The silica impurity decreases the activation energy of the initial stage of sintering and grain boundary energy, improves the densification process and exerts a moderate inhibitor effect on the grain growth.

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INTRODUCTION

It is well established that small amounts of additives can have a great influence on the sintering of a ceramic powder. Solute additions may modify the defect structure of the solvent, form a solid second phase which pins grain boundaries, form a liquid phase, or segregate at grain boundaries reducing boundary mobility. The most extensive studies on alumina have focussed on the effect of dopants that go in solid solutions, such as TiO_2 ¹ and MgO .^{2,3} Silica is one of the most common substances found associated with commercial alumina. However, no systematic study of the possible effect of this impurity, either in ceramic processing or in the sintering behavior of alumina powder, has been carried out. In the present study the emphasis was placed on evaluating the compactability, sintering behavior and microstructure development of a typical alumina powder with and without silica as the principal impurity.

EXPERIMENTAL

A. Powder Preparation, Filtering and Pressing

Alumina powder with a particle size ranging from 2 to 5 μm was used.* X-ray analysis showed only α -alumina. It was submitted to the following treatments:

- a) 25 g. were treated with 500 ml. of 0.2 N HF for 2 hrs with constant shaking, filtered and washed with triple-distilled water (spectrographic analyses of the untreated and HF-treated powders are given in Table I);

*Alcoa A-14 alumina powder.

- b) Slurries of HF-treated and untreated powder were prepared in polyethylene bottles with a concentration of 25 g./lt. and a pH of ~4.5 (high zeta potential) by adding HClO_4 and exposed to constant shaking for 48 h. (their filtering behavior was studied with Sybron Nalge 0.2 μm filters using a vacuum rotative pump); and
- c) the cakes were dried at 60°C for 48 h. after washing with distilled water (these dry powders were used in the pressing and sintering studies after brushing but without any mechanical grinding).

The pressing behavior of both powders heat-treated at 60, 850 and 1180°C was studied using a die with a 0.5 in. diameter. The walls of the die were lubricated with a stearic acid solution. A pellet's thickness was measured after pressing a constant amount of powder to a given pressure by measuring the height of the pressing ram with a dilatometer dial with an error of $<10^{-4}$ in.

B. Sintering

Pellets (0.5 in. diameter and 0.09 in. thick) with 55.5 or 60.0% theoretical green density were prepared. At least two specimens for each powder at each sintering thermal treatment were used.

A bottom-loading type furnace with MoSi_2 heating elements was used for the sintering anneals in air. Runs were made at 1300, 1400, 1500 and 1650°C for varying times. Specimens prepared from HF-treated and untreated powders were fired together in a platinum crucible placed on a refractory pedestal which was raised into the furnace at a rate equivalent to ~35°C/min. up to 1215°C. The specimens were then raised to the hottest portion quickly and reached the sintering temperature within 20 min. This point was considered as zero time. The time at constant temperature ranged from zero minutes to 28 hrs. After each sintering

run the pellets were cooled to 1100°C within 10 minutes by switching off the furnace as well as lowering the pedestal from the hot zone and then cooling in air to room temperature.

The diameter shrinkage after each isothermal treatment was measured with a micrometer with an error of $<2 \times 10^{-4}$ in. The sintered average bulk density was determined according to the following relationship:

$$\rho_i = \frac{\frac{n}{Z} \rho_o \left(1 - \frac{\Delta L}{L_o}\right)^3}{n} \quad (1)$$

where ρ_o is green density of the specimen, and $\frac{\Delta L}{L_o}$ is fractional shrinkage. At least ten measurements on each specimen were used to provide an average bulk density. The maximum deviation from the average values was not greater than 5 percent. The total porosity was then calculated on the basis of a theoretical density for Al_2O_3 of 3.97 g/cm^3 .

C. Microstructure Analysis

Samples from the filter cakes were examined by scanning electron microscopy (SEM). Selected specimens sintered at 1650°C were polished, thermally etched at 1400°C for 3 hrs. and examined by SEM. The average grain size was determined by the intercept method using random straight lines drawn directly on the microphotographs.⁴

RESULTS

Figure 1 represents the cumulative filtrate volume (V) through one cm^2 of the filter versus time (t) for the HF-treated and untreated alumina powder slurries. Assuming that the cakes are incompressible, the following equation can be considered:⁵

$$\frac{dt}{dV} = \alpha \mu C \frac{V}{A^2 \Delta p} + \frac{\mu R}{A \Delta p} \quad (2)$$

where α is specific cake resistance, μ is viscosity of filtrate, C is concentration of solid in the suspension, R is medium resistance, A is filter areas, and Δp is pressure drop. If Δp is constant, (2) can be integrated and expressed as

$$\frac{t-t_s}{V-V_s} = \frac{\alpha\mu C}{2A^2\Delta p} (V + V_s) + \frac{\mu R}{A\Delta p} \quad (3)$$

where t_s and V_s represent the point at the beginning of the truly constant pressure period. Equation (3) shows a linear dependency between $t-t_s/V-V_s$ and V where the slope is proportional to α .

Applying the data from Fig. 1 to Eq. (3) a linear behavior is observed as shown in Fig. 2. From the slopes of the straight lines the ratio between the specific cake resistance with HF-treated (α_T) and untreated (α_u) powders is $\alpha_T/\alpha_u = 6.7$. SEM microphotographs of fractured cross sections of the filter cakes after drying at 60°C for 48 h. are shown in Fig. 3.

The fractional theoretical green density of pellets formed from HF-treated and untreated powders as dried at 60°C and thermally treated at 850 and 1180°C versus pressure is shown in Fig. 4.

Figure 5 presents the porosity versus time data as 1300, 1400 and 1500°C. All the specimens had a starting unfired porosity of 44.5%. The isothermal curves show an initial straight line. In terms of the sintering kinetics model proposed by Wong and Pask,⁶ this fact suggests that the controlling or slow step for densification in the initial stage of sintering consists in the movement of material from the neck areas to the free surfaces. The equation for this initial stage of sintering is

$$P - P_0 = -K(t-t_0) \quad (4)$$

and

$$K = \frac{A_1 D_B \Omega \gamma_{SV} N^3}{kT}$$

where A is a proportionality constant, P is the porosity, t is the sintering time, D_B is the bulk diffusion coefficient, Ω is the atomic (molecular) volume, γ_{SV} is the specific surface free energy at the solid-vapor interface, T is the absolute temperature, k is Boltzmann's constant, P_0 and t_0 are the initial porosity and time on reaching the test temperature T, and N is the number of interconnected voids per unit volume which remains constant during this stage. N is inversely proportional to grain size which determines the number of grains per unit volume for a given packing.

Sintering rate coefficients K, were determined according to Eq. (4) from the slopes of the linear portion of the curves in Fig. 5 and plotted in Fig. 6 as log K versus the reciprocal of absolute temperature. The activation energies were determined to be 67 Kcal/mol for untreated and 88 Kcal/mole for HF-treated powder.

The microstructure of pellets sintered at 1650° was examined. The unfired density in this case was 60% theoretical. For a given firing condition the final density was higher for the pellets formed with untreated than for those with treated powder. SEM microphotographs for pellets sintered for 28 hrs after polishing and thermally etching are shown in Fig. 7. The density for the untreated powder pellets was 91% and for the HF-treated pellets, 88% theoretical. The corresponding average grain sizes were 3.5 μ m and 3.9 μ m, respectively. Grain boundary groove width measurements were made by using high magnification (20,000X)

SEM microphotographs; the values were $0.15 \pm 0.05\mu\text{m}$ and $0.40 \pm 0.05\mu\text{m}$, respectively.

DISCUSSION

The indicated HF-treatment caused the removal of ~95% of the silica impurity as seen in Table I. This fact indicates that almost all of the silica impurity is present on the surface of alumina powder and must exist in a free active form, because mullite is not subject to this solution.

In a previous study, Moya et al.⁷ reported that silica impurity shifts the isoelectric point of the alumina powder to the acid pH region causing the alumina to behave as a silica-like compound from electrophoretic point of view. This study further showed that in either case the treatment of the powder at a low pH caused a high Z-potential which kept the powder dispersed and retarded the formation of agglomerates.⁸ Hence, the purpose of the treatment at a pH of ~4.5.

On immersion of both powders in water, the development of an electric double layer at the oxide/water interface takes place. The structure and configuration of the hydroxyl layer that forms must be determined by the nature of particle surface. In the case of the untreated or silica-bearing alumina surface the OH total population must be close to $4.6/\text{nm}^2$ which corresponds to a fully hydroxylated silica surface.⁹ When the silica is removed by HF-treatment, alumina surface is obtained and consequently a higher population of OH is expected ($\sim 10/\text{nm}^2$).

In addition, according to Knozinger and Ratnasamy,¹⁰ five possible OH configurations can occur on an alumina surface, the actual occurrence

and concentration depending on the exposed crystal face. Each configuration is characterized by a different level of acidity or basicity. In the alumina powder treated with HF acid, different crystal faces can be expected to manifest themselves and they would also be expected to have different hydroxyl layer structures. Thus, when the alumina particles come in contact during the cake formation, the OH basic and acid can react to form water bridges or structured water that keeps the particles bonded in a packing with high coordination number. In Fig. 3 (a) the possible appearance of such a structure can be observed.

In the case of untreated powder, the OH population of the hydroxyl layer on the "silica-like" surface is less and all of the surfaces would be expected to be similar and protonic in nature.¹¹ Therefore, the surfaces are not as reactive and the particles form a more open cake structure, as seen in Fig. 3 (b); isolated particles appear to be present. The observed differences in structure and packing provide an explanation for the differences in the specific cake resistances to filtering; the cake formed from the HF-treated powder being more resistant as determined experimentally.

The pressing behavior of both powders (Fig. 4) can also be explained on the basis of the observed structures in Fig. 3. The requirement of less pressure to obtain a compact with a given density and the higher compactability of the HF-treated powder suggest that the hydroxylated layers must be subject to deformation by shear. Treatment at 850 and 1150°C reduces this capability. Almost complete dehydroxylation takes place in this temperature range.¹² However, during the handling of the powder after heat treatment, a partial rehydroxylation may

have taken place* which was responsible for its intermediate behavior. Presumably the untreated powder surface did not have a similar surface and shear capability as indicated by the fact that a heat treatment at 850°C did not have any effect on its pressing behavior and that considerably higher pressures were necessary to obtain equivalent densities.

A lower bulk porosity at zero time (P_0) than the unfired value of 0.445 indicates that some densification has occurred in reaching the isothermal experimental temperature. The smaller value for the HF-treated powder than for the untreated powder at all temperatures (Fig. 5) can be due to a particle rearrangement phenomenon caused by the loss of the structural water during the heating period.

The apparent activation energy values of 67 Kcal/mole for untreated and 88 Kcal/mole for HF-treated powders determined in this study for the initial stage of sintering are much smaller than the 150 Kcal/mole and 114 Kcal/mole values corresponding to oxygen-ion diffusion¹³ and aluminum-ion diffusion¹⁴ in alumina, respectively. This study's data, however, are in agreement with the 75 Kcal/mole value obtained by Wang¹⁵ for a similar type of powder for the initial stage of sintering (below 2.5% fractional shrinkage). It is difficult to provide an explanation for the different values at the present time. The smaller activation energy value obtained for untreated powder may be associated with the nature of the silica impurity. The surface form may enhance diffusivity which in turn enhances the sinterability and decreases the activation energy.

*Berkeley Lab. relative humidity was about 75% during the experimental period.

It has been reported in the literature^{13,16} that the sintering of stoichiometric oxides such as aluminum oxide and magnesium oxide, may be dramatically affected by an additive that will enter the solid solution and disturb the oxide stoichiometry. However, this is not the case in the present system. The silica may be considered almost completely insoluble in aluminum oxide and must therefore be segregated in the grain boundary as some kind of disordered phase. According to Yan, et al.¹⁷ the presence of a liquid film in the grain boundary can give relatively high rates of grain growth. On the other hand, Cutler¹⁸ suggests that additives forming a second phase without the formation of a liquid apparently inhibit the densification process.

The data obtained in the present investigation show that the silica impurity enhances the densification process and exerts a moderate inhibitor effect on the grain growth.

The width of the groove was about two times larger for the HF-treated than for the untreated sample. This fact suggests that the specific grain boundary energy γ_{gb} is larger in the former case. Assuming that the net curvature of grain boundary (r) is about the same in both samples (Fig. 7) and taking into account the expression¹⁹ $P = \gamma_{gb}/r$, where P is the driving force for grain boundary motion, a larger driving force will be expected in the HF-treated sample and consequently a larger average grain size, which is in agreement with the experiments.

CONCLUSION

A silica impurity is present on the surface of the alumina powder used, and it can be essentially removed by HF acid treatment. The present study shows that the silica plays a significant role both in the

ceramic processing of alumina powders and in the sintering and micro-structure development of the alumina compacts.

Presence of a surface silica impurity affects the compactibility of the powder adversely. It increases sintering densification and decreases the activation energy.

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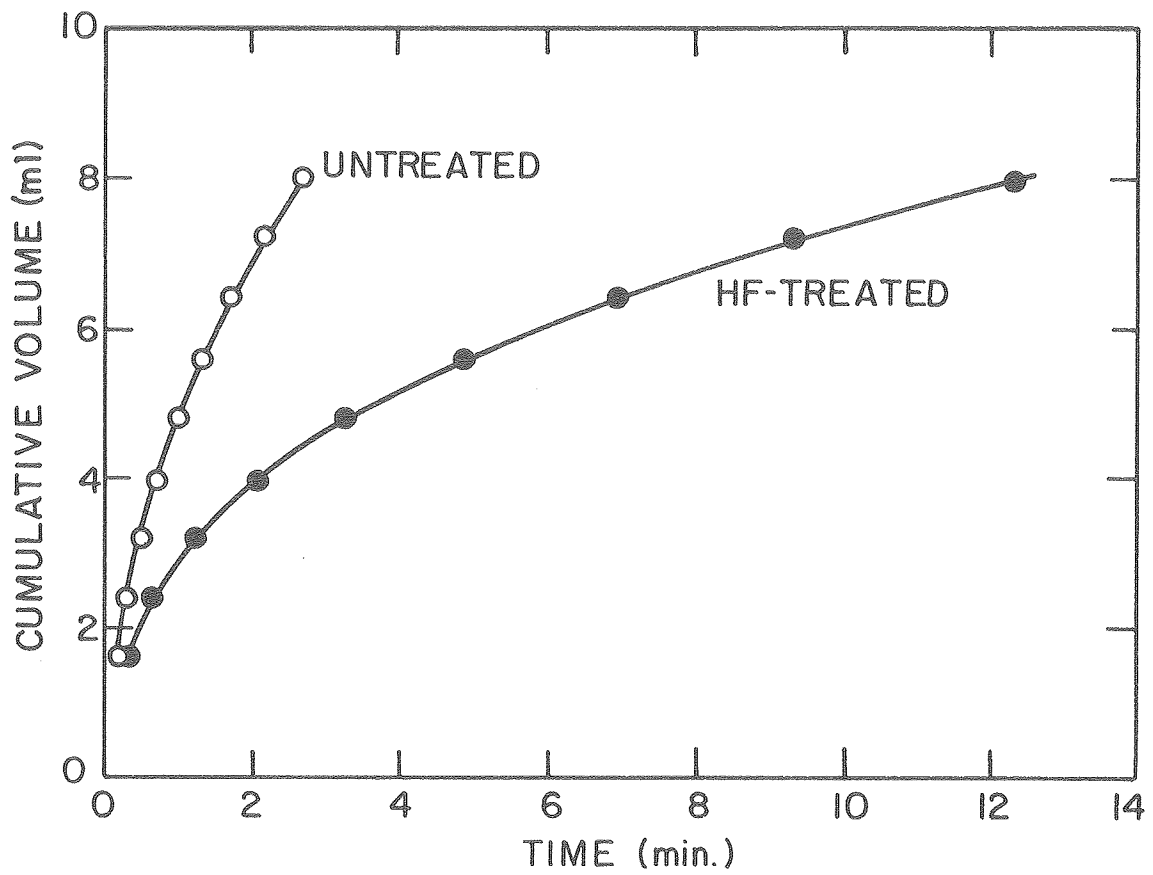
Table I. Spectrographic Analysis Data of Alumina Specimens

Constituents*	Untreated (%)	HF-treated (%)
Al	Principal constituent in each sample	
Si	0.15	0.01
Ca	0.01	0.005
Fe	0.04	0.03
Mg	0.005	0.003
Ga	0.008	0.007
Ti	0.003	0.002
Ba	0.001	-
Cu	0.001	0.001

*Constituents reported as oxides of the elements indicated. Analysis performed by American Spectrographic Laboratories Inc., San Francisco, California.

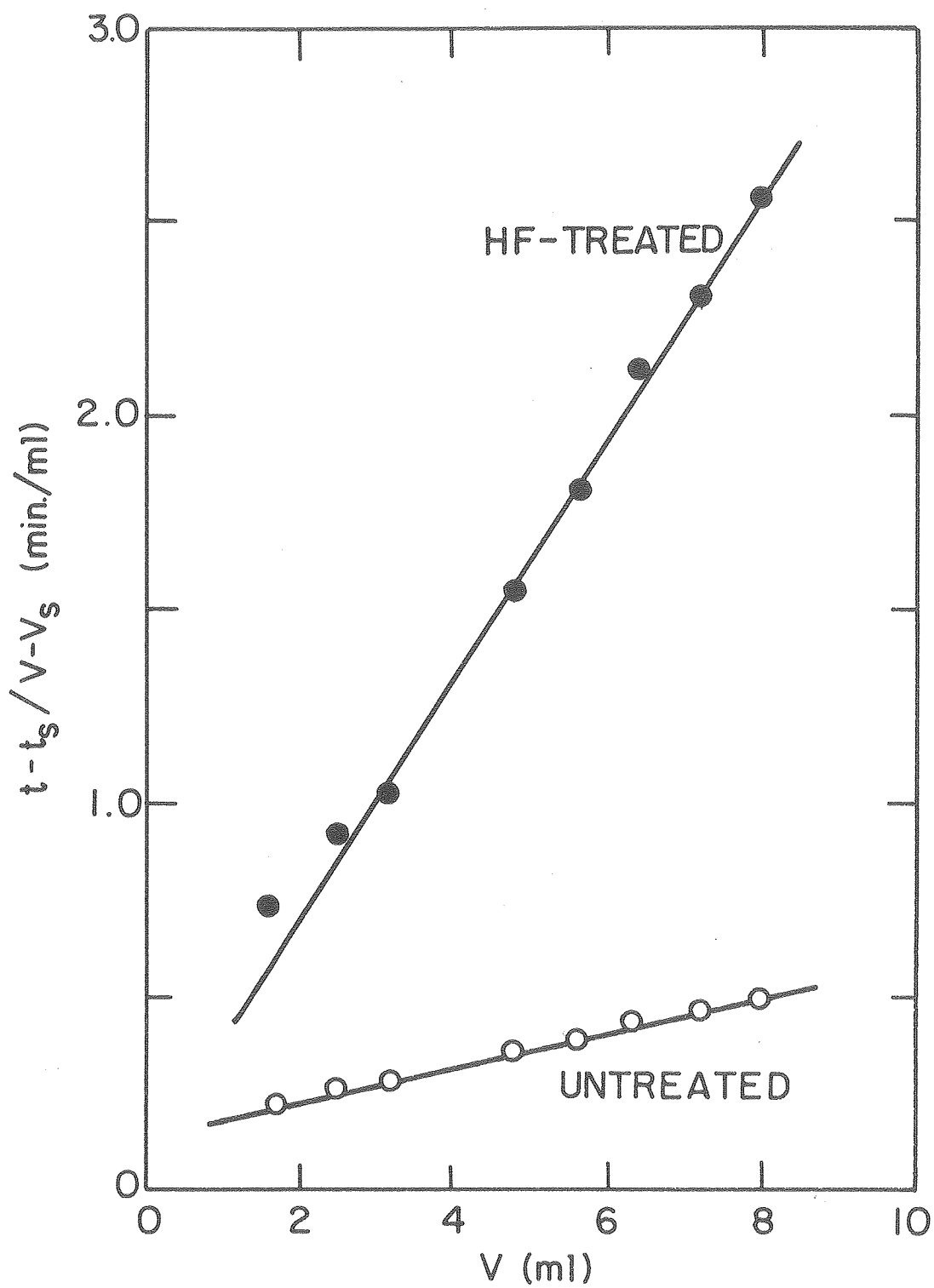
FIGURES

- Fig. 1. Cumulative filtrate volume (V) vs. time for HF-treated and untreated alumina powders.
- Fig. 2. $t-t_s/V-V_s$ vs. cumulative filtrate volume (V) for HF-treated and untreated alumina powders.
- Fig. 3. SEM micrographs from fractured cake cross-sections for HF-treated (A) and untreated (B) powder at several magnifications.
- Fig. 4. Relative compact green density vs. pressure for HF-treated and untreated powders heated at indicated temperatures.
- Fig. 5. Porosity vs. time for HF-treated and untreated compacts sintered isothermally in air at indicated temperatures.
- Fig. 6. Rate constants vs. $1/T$ for HF-treated and untreated compacts.
- Fig. 7. Microstructures of polished surfaces for HF-treated (A) and untreated (B) compacts sintered in air at 1650°C for 28 hrs. obtained by SEM.



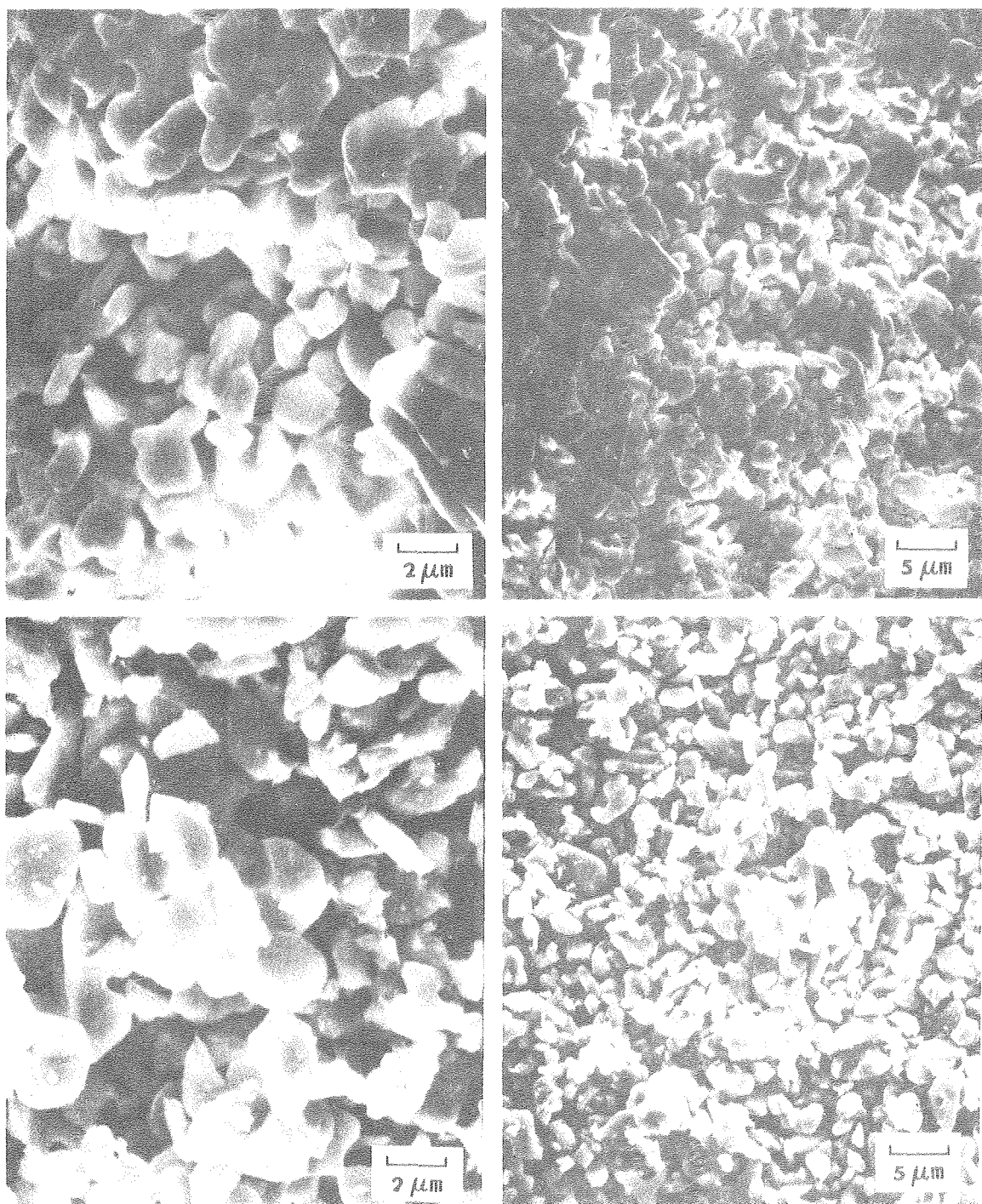
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Fig. 1



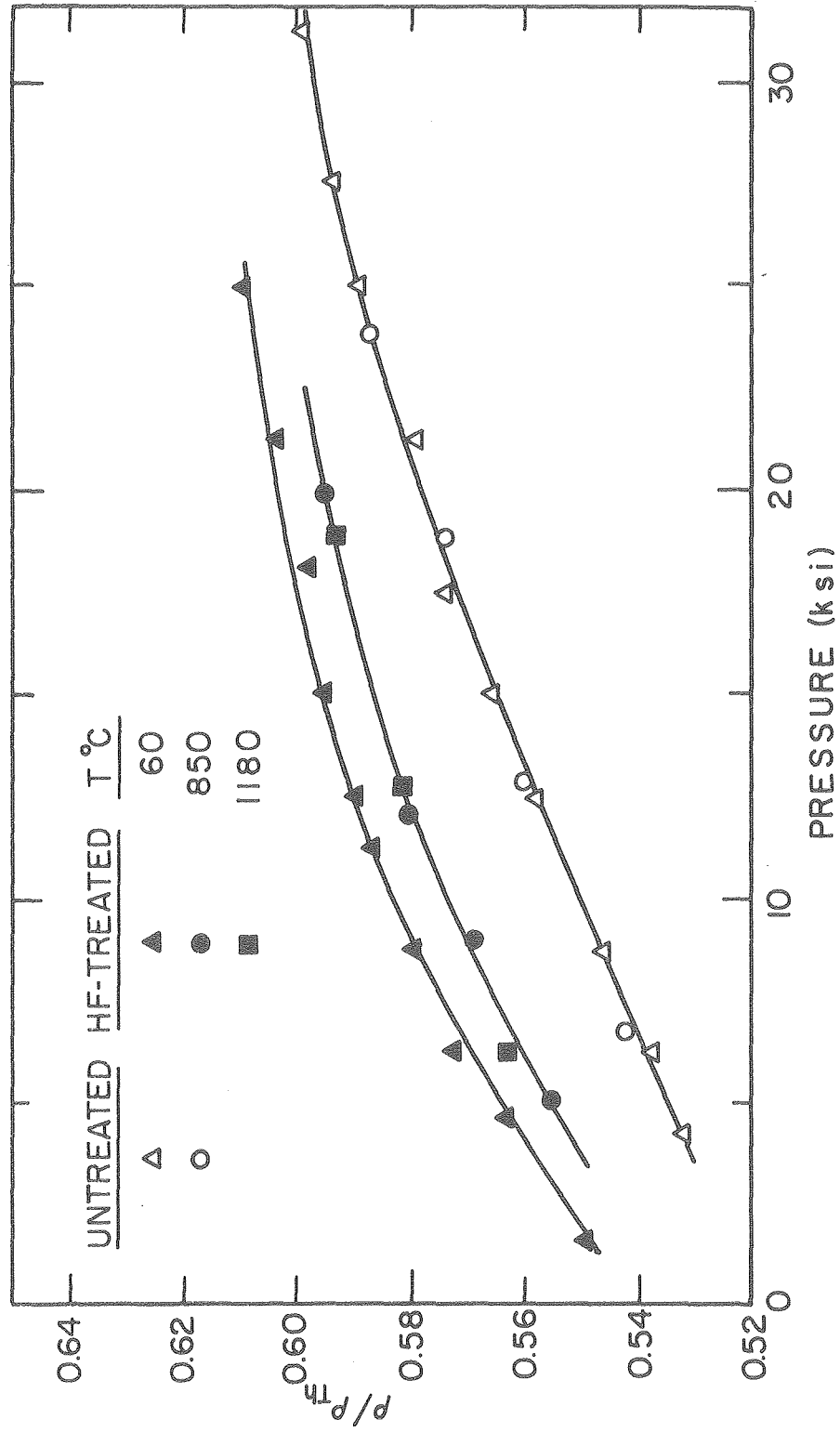
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Fig. 2



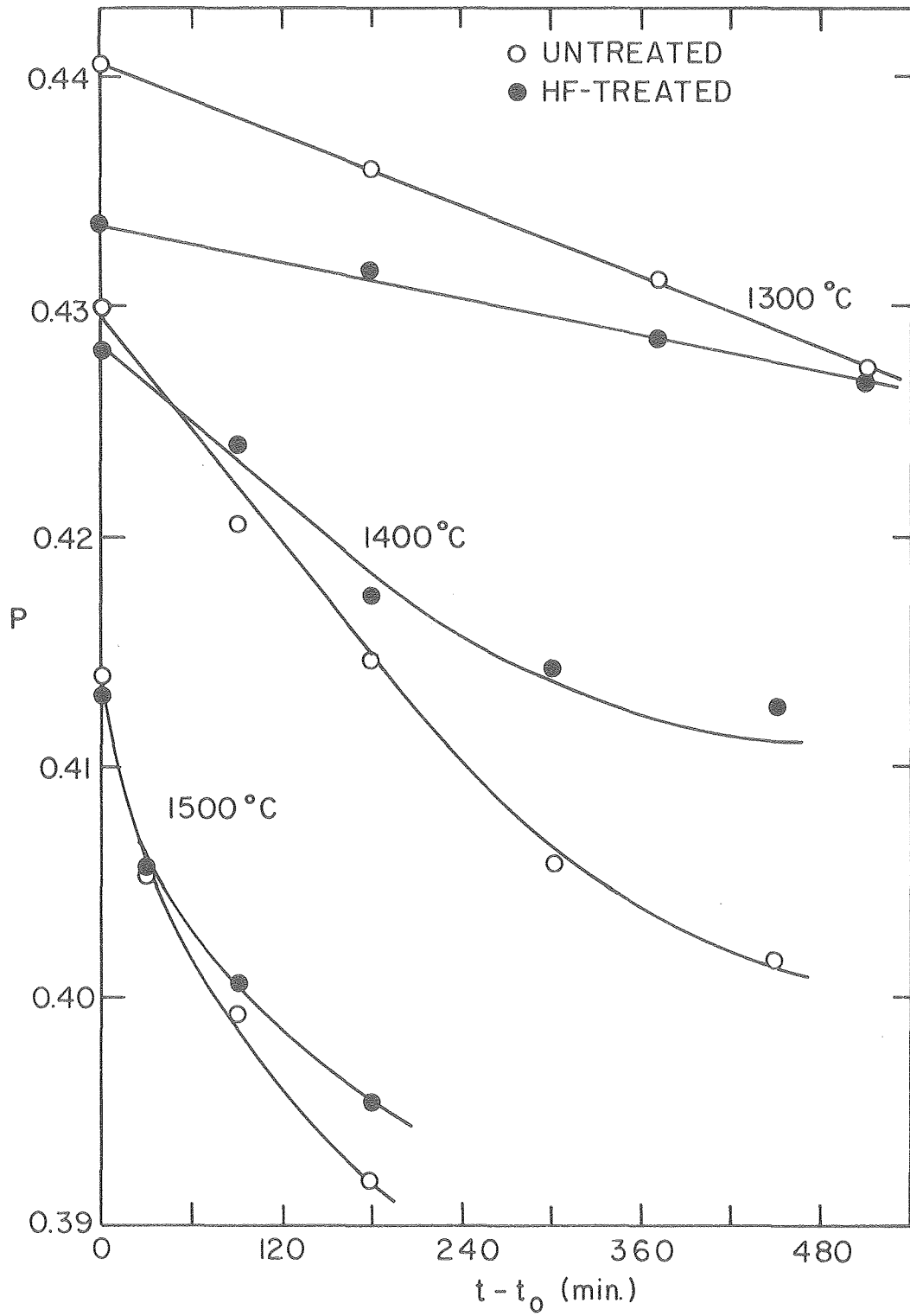
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Fig. 3



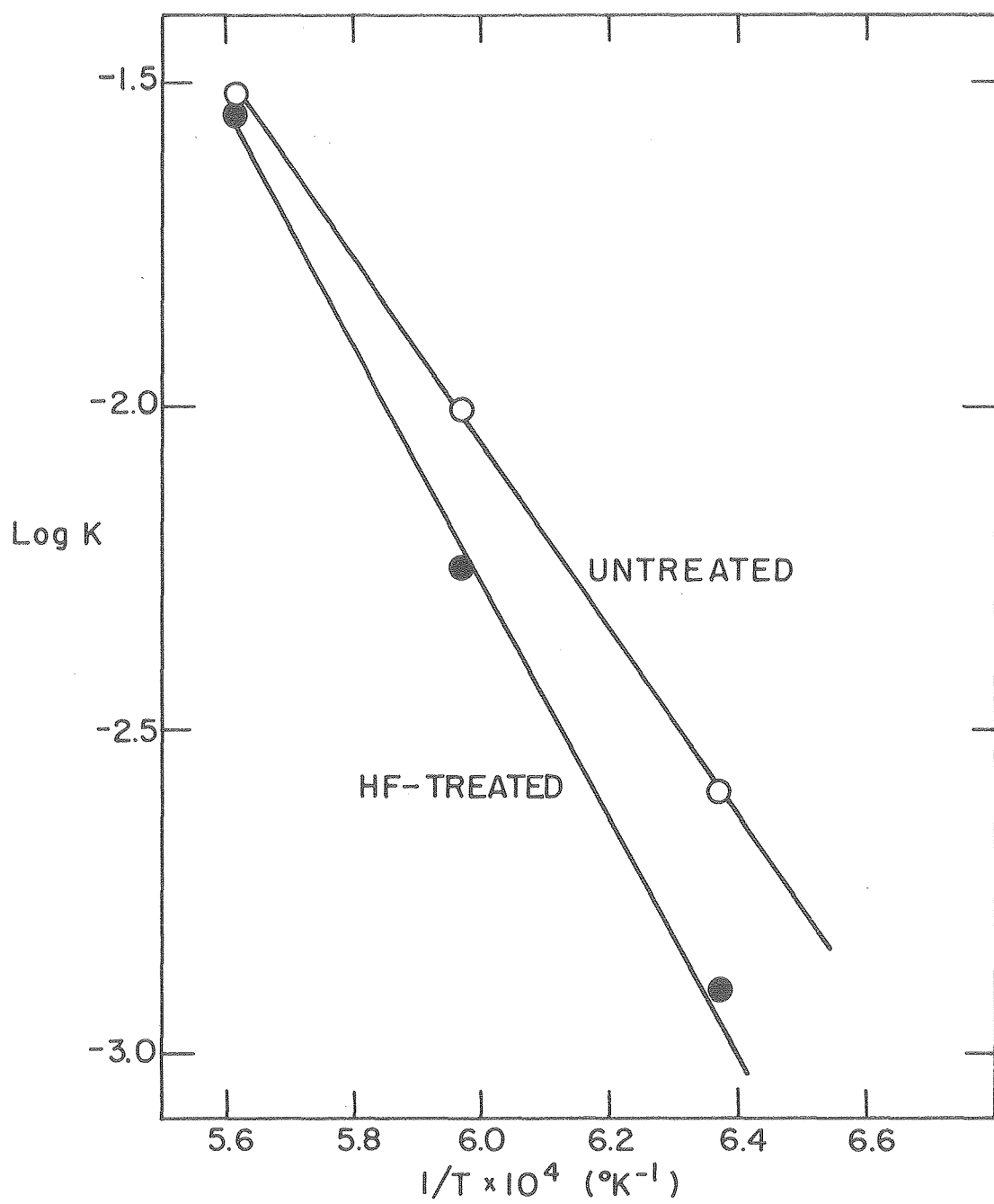
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Fig. 4



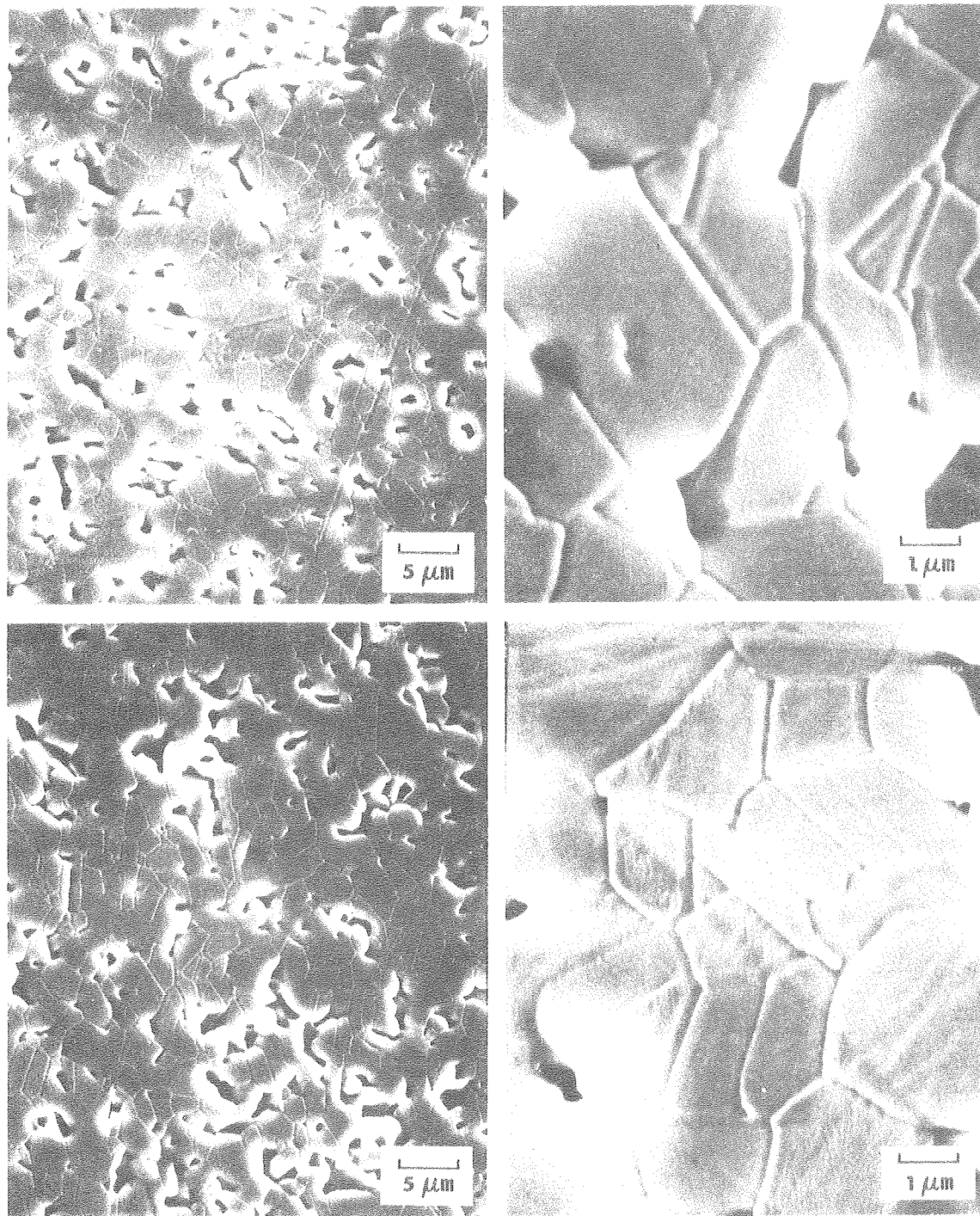
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Fig. 5



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Fig. 6



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Fig. 7